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(71) Applicant(s)

Merck Patent GmbH

(Incorporated in the Federal Republic of Germany)

Frankfurter Strasse 250, D-64271 Darmstadt,
Federal Republic of Germany

(72) Inventor(s)

David Coates
Simon Greenfield

(74) Agent and/or Address for Service

Venner Shipley & Co
20 Little Britain, LONDON, EC1A 7DH,
United Kingdom

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(54) Composite liquid crystal - polymer material

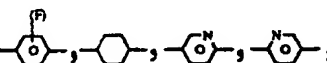
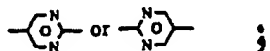
(57) The invention refers to a composite material comprising a liquid crystal material (with a birefringence $\Delta n = n_e - n_o$) and a polymeric medium (which is optically substantially transparent and isotropic and has a refractive index of n_m) wherein either the liquid crystal material is embedded in microdroplets in the polymeric medium (with one of the refractive indices of the liquid crystal material being substantially matched to the refractive index n_m of said polymeric medium) or the liquid crystal material is present as a substantially continuous phase in a 3-dimensional network formed by or with the polymeric medium, the composite being characterized in that the liquid crystal material contains at least one compound of formula I



[wherein


R^1 is alkyl with 1-6 C atoms, wherein one or two CH_2 -groups can be replaced by -O- or -CO-;

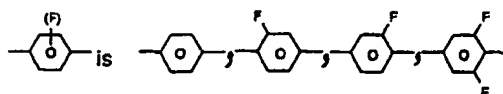
R^2 is alkylene $(CH_2)_p$ - with p ranging from 1-6, wherein one or two CH_2 -groups can be replaced by -O- or -CO-;

A is independently from each other  ;
 ;

Z is independently from each other a single bond, - CH_2-CH_2 -, -COO- or -OCO-;

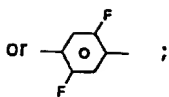
m is 1, 2 or 3;

B is  ;



(57) continued overleaf

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R³ is F, Cl, CN, X-G;

X is a single bond, -O- or -S- ;

G is Me or Et where one or more H may be replaced by F;

with the proviso that at least one of A and B is a laterally mono- or difluorinated 1,4-phenylene group].

The precursor of the composite material is also claimed, namely a composition comprising a liquid crystal material (which contains at least one compound of formula I) and a UV-curable precursor of the polymeric medium.

Composite material

5 The invention relates to a composite material comprising a liquid crystal material with a birefringence $\Delta n = n_e - n_o$, and a polymeric medium, which is optically substantially transparent and isotropic and has a refractive index of n_m , the liquid crystal material being embedded in microdroplets in the polymeric medium with one of the refractive indices of the liquid crystal material being substantially matched to the refractive index n_m of said polymeric medium, or the liquid crystal material being present as a
10 substantially continuous phase in a 3-dimensional network formed by or with the polymeric medium.

15 Depending on the mass content of the liquid crystal mixture in the composite material, this can be embedded in the optically transparent medium in liquid crystal microdroplets which are separated to a greater or lesser extent from one another or else form a more or less coherent, continuous phase in which the optically transparent medium is present, for example, in the form of particles. A continuous phase is also obtained, for example, if the optically transparent medium forms a sponge-like, 3-dimensional
20 network whose pores, in which the liquid crystal is located, merge into each other to a greater or lesser extent. The expression liquid crystal microdroplets here indicates small liquid crystal compartments separated from one another which, however, in no way have to have a spherical shape, but can be irregularly shaped and/or deformed.

25 If the optically transparent medium contains liquid crystal microdroplets, it is described in the following as a matrix; on the other hand, if a more or less continuous phase of the liquid crystal is present, the medium is described by the expression network.

30 NCAP and PDLC films (NCAP = nematic curvilinear aligned phases, PDLC = polymer dispersed liquid crystal) are examples of electrooptical liquid crystal systems in which the liquid crystal is embedded in the matrix in the form of microdrops.

35

NCAP films are usually obtained by intimately mixing the encapsulated polymeric material, such as, for example, polyvinyl alcohol, the liquid crystal mixture and a carrier material, such as, for example, water, in a colloid mill. The carrier material is then removed, for example by drying.
5 An appropriate process is described in US 4,435,047.

In contrast, the liquid crystal mixture is first homogeneously mixed with monomers or oligomers of the matrix-forming material in the preparation of PDLC films described, for example, in US 4,688,900, Mol. Cryst. Liq.
10 Cryst. Nonlin. Optic, 157, (1988), 427-441, WO 89/06264 and EP 0,272,585. The mixture is then polymerized and the phase separation is induced (so-called PIPS technology; polymerization-induced phase separation). In addition, differentiation must further be made between TIPS (temperature-induced phase separation) and SIPS (solvent-induced phase
15 separation) (Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt. 157, (1988) 427).

The process of preparation of PDLC films must be controlled very carefully in order to obtain composite materials with good electrooptical properties. F.G. Yamagishi et al., SPIE Vol. 1080, Liquid Crystal Chemistry, Physics
20 and Applications, 1989, p. 24 differentiate between a "Swiss cheese" and a "polymer ball" morphology. In the latter one, the polymer matrix consists of small polymer particles or "balls" being connected or merging into each other while in the Swiss cheese system, the polymer matrix is continuous and exhibits well defined, more or less spherical voids containing the liquid
25 crystal. The Swiss cheese morphology is preferred because it exhibits a reversible electrooptical characteristic line while the polymer ball system shows a distinct hysteresis generally leading to a drastic deterioration of the electrooptical characteristic line when comparing the virgin and the second run.

30 According to Yamagishi et al., loc. cit., the Swiss cheese morphology is promoted in case the polymerization reaction runs via a step mechanism, and in WO 89/06264 it is pointed out that the step mechanism is favoured in case the precursor of the polymer matrix consists of multifunctional
35 acrylates and multifunctional mercaptanes.

5 The PN system (PN = Polymer Network) described in EP 0,313,053 has a sponge-like network structure of the optically transparent medium. The content of the liquid crystal mixture in the material of the light-modulating layer is in general greater than 60 % in systems of this type and is, in particular, between 70 and 90 %. In order to prepare the PN systems, a mixture of the liquid crystal, monomers or oligomers of the material forming the 3-dimensional network and a polymerization initiator, in particular a photoinitiator, is customarily brought between 2 substrate plates provided with electrodes and then polymerized, for example by light irradiation.

10 The liquid crystal in general has a positive dielectric anisotropy $\Delta\epsilon$ and a relatively high optical anisotropy. In microdroplet matrix materials, one of the refractive indices of the liquid crystal, customarily the ordinary refractive index n_o is selected in such a way that it more or less coincides with the refractive index n_M of the polymeric matrix. In the case of network materials, and adjustment of the refractive indices owing to the customarily very much higher liquid crystal content in the light-modulating layer is not absolutely necessary, but can be carried out to increase the light transmission and the contrast.

20 Arranging the composite material between 2 electrode layers yields an electrooptical system with an electrically switchable light scattering effect.

25 If not voltage is applied to the electrodes, light incident on the statistically aligned liquid crystal molecules is strongly scattered and the system is non-transparent. On applying a voltage, the liquid crystal molecules are aligned parallel to the field and perpendicular to the E vector of the transmitted light.

30 In the case of microdroplets matrix materials, perpendicularly incident light sees an optically isotropic medium when voltage is applied owing to the adjustment of n_o and n_M and the system appears transparent. An adjustment is necessary in order to avoid a scattering of the light at the

35

5 matrix/liquid crystal droplets phase boundary. EP 0,272,585 describes another embodiment in which the refractive index n_x , which the liquid crystal exhibits at completely statistical orientation, is adjusted to the refractive index of the matrix n_M . In this case, the system is transparent in the field-free state, and it is converted into the opaque state by applying a voltage.

10 In the case of network materials, an adjustment of the refractive indices is not absolutely necessary, as owing to the high liquid crystal content in the material of the light-modulating layer, the scattering at the network/liquid crystal phase boundary is obviously less strong. In the switched-on state, the material appears transparent even without adjustment of the refractive indices. In the case of network materials, the use of liquid crystals having high optical anisotropy is preferred to achieve a transmission which is as low as possible in the non-connected state.

20 In WO 89/09807, the use of an optically anisotropic, for example liquid crystalline polymeric matrix material has been proposed in order to avoid the frequently observed clouding ("haze", in particular "off-axis haze") in the transparent state of the system. In systems of this type, the refractive indices of liquid crystal and optically anisotropic matrix can be adapted to each other so that the transparent state is obtained either with the voltage applied or switched off.

25 Composite materials according to the preamble of Claim 1 have been especially proposed for large-surface-area indicating systems, for architectural applications (windows, room dividers, sunroofs etc.) and for motor vehicles (windows, sunroofs etc.), these systems also being suitable for temperature regulation by virtue of controlled screening of the solar radiation. They can be switched on by applying a direct or alternating voltage.

35

Examples of other applications are:

- 5 - GH-indicating systems, the spectrum extending from simple segment displays to displays, to which it is possible to apply any desired electrode pattern using conventional printing techniques.
Applications: motor vehicles, large displays, advertizing boards, clocks
- 10 - displays having a high information content controlled by active or passive matrix
- 10 - projection systems
- switches

15 Composite materials according to the preamble of claim 1 are complex systems, and there has been considerable effort in the recent past to improve the polymeric medium forming the matrix resp. the network, the liquid crystal material, the method of preparation and further features of such materials.

20 Improved liquid crystal mixtures for use in said composite materials have been proposed, for example, in WO 91-05,029 while improved materials to be used as polymeric medium are described, for example, in JP 92-337,385, JP 93-105,878, EP 0,541,912 and WO 93-09,202. All these reference emphasize the complex relationship between the different

25 components of the composite material and stress the necessity to improve to interaction of the various components of such materials in the uncured precursor state and in the cured state of the composite material.

30 In view of the broad range of applications of the composite materials it was desirable to have available further materials of this type which fulfill the various requirements such as a broad working temperature range, a high solubility of the liquid crystal in the uncured precursor of the polymeric

5 medium and a low solubility of the liquid crystal mixture in the cured poly-
meric medium, a good processibility and good electrooptical properties
like, for example, a high transmission, low switching voltages, no
hysteresis, a high holding ratio, reasonable switching times etc. to a
satisfactory and/or high degree.

10 The composite materials hitherto known often exhibit values of switching
voltages which are too high for many applications. Using the composite
materials, for example, for windows or other architectural applications,
rather low values of the operating voltages are desired in order to reduce
power consumption and to increase safety of operation. In case of high in-
formation content PDLC displays driven by an active matrix, $V_{90,20,45}$
(= voltage producing in an electrooptical system a transmission of 90 % at
20 °C and a viewing angle of 45°) should be not higher than 15 V,
15 preferably, however, less than 12 V in order to establish compatibility with
commercially available IC driving circuits.

20 In US 4,673,255 it is shown that a correlation exists between the mean
size of the microdroplets on the one hand and the switching voltages and
switching times of the system on the other hand; experimental methods for
influencing the average droplet size are described, for example, in
US 4,673,255 and in J.L. West, Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.,
157, 1988, 427.

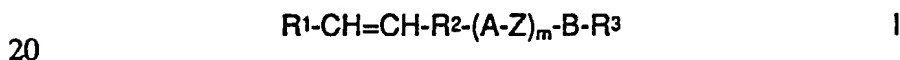
25 An improvement of the switching voltages at the cost of switching times is,
however, generally only tolerable to a limited degree what is evident in the
case of display applications but what is also true for many other applica-
tions.

30 The switching voltages can furthermore be improved by reducing the thick-
ness of the composite material film which, however, at the same time
results in a decrease of contrast.

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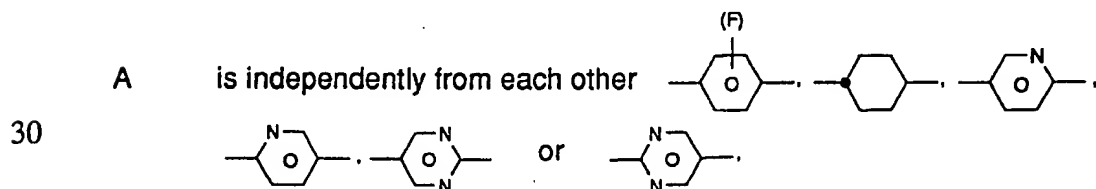
It was an object of the present invention to provide composite materials and electrooptical systems comprising such composite materials which exhibit low to very low driving voltages which at the same time fulfill the other requirements listed above to satisfactory and/or good degree and, in particular, exhibit acceptable to good switching times and an acceptable to high contrast. Other objects of the present invention can be taken from the following detailed description.

The present invention thus relates to composite materials, comprising a liquid crystal material, with a birefringence $\Delta n = n_e - n_o$, and a polymeric medium, which is optically substantially transparent and isotropic and has a refractive index of n_m , the liquid crystal material being embedded in microdroplets in the polymeric medium with one of the refractive indices of the liquid crystal material being substantially matched to the refractive index n_m of said polymeric medium, or the liquid crystal material being present as a substantially continuous phase in a 3-dimensional network formed by or with the polymeric medium, characterized in that the liquid crystal material contains at least one compound of formula I



wherein

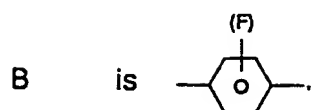
25 R¹ is alkyl with 1-6 C atoms, wherein one or two CH₂-groups can be replaced by -O- or -CO-,
R² is alkylene -(CH₂)_p- with p ranging from 1-6, wherein one or two CH₂-groups can be replaced by -O- or -CO-,



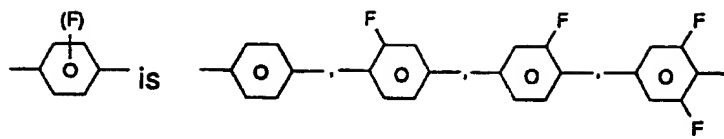
Z is independently from each other a single bond, -CH₂-CH₂-, -COO- or -OCO-,

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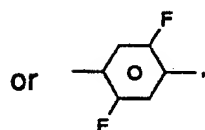
m is 1, 2 or 3,



5



10



R³ is F, Cl, CN, X-C_rH_sF_{2r+1-s},

15

X is a single bond, -O- or -S-,

r is 1 or 2,

20

s is 0, 1, 2, 3, 4 or 5

with the proviso that at least one of A and B is a laterally mono- or difluorinated 1,4-phenylene group.

25

The invention furthermore relates to electrooptical systems containing a film of the composite material according to the invention between 2 electrode layers, and to a process for the preparation of such systems.

30

The construction of the composite material and the electrooptical liquid crystal systems according to the invention corresponds to the customary mode of construction for materials and systems of this type. The term customary mode of construction is in this case broadly interpreted and includes all adaptations and modifications.

35

Thus for example, in the case of PDLC and NCAP films, the matrix formed by the transparent polymeric medium in which the liquid crystal mixture is microdispersed or microencapsulated is arranged between conducting electrodes like a sandwich.

5

The electrodes are applied, inter alia, to substrate sheets of, for example, glass, plastic or the like; if desired, however, the matrix can also be provided directly with electrodes so that the use of substrates can be avoided,

10

In the case of network materials, the liquid crystal is usually located in the pores of the sponge-like, 3-dimensional network. The network is customarily arranged between substrates provided with electrodes in order to prevent escape of the liquid crystal.

15

Both network and microdroplets matrix materials can be operated reflectively or transmissively so that at least one electrode and, if present, the associated substrate are transparent. Both systems customarily contain no polarizers, as a result of which a distinctly higher light transmission results. Furthermore, nor orientation layers are necessary, which is a considerable technological simplification in the production of these systems compared with conventional liquid crystal systems such as, for example, TN or STN cells.

20

25

In the literature, there are various details about materials suitable for the production of the polymeric medium.

Thus, for example, in US 4,435,047 or in Liquid Crystals, 3, (1988), 1543, water-soluble polymers are proposed, such as, for example, polyvinyl alcohol PVA or latex-like emulsions, for the preparation of matrix materials of NCAP type.

30

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The PDLC systems described in Mol. Cryst. Liq. Cryst. Inc. Nonlin. Optics, 157, 427 are based on an epoxy film, while in EP 0,272,585 acrylate systems are given. The PDLC system of WO 89/06264 is based on multifunctional acrylates and multifunctional thioles, and Y. Hirai et al., SPIE Vol. 1257, Liquid Crystal Displays and Applications, 1990, p. 2 describe PDLC systems the precursor of the polymer matrix of which being based on monomers and oligomers. Further suitable matrix materials are described, for example, in JP 92-337,385, JP 93-105,878, EP 0,541,912 and WO 93-09,202.

For the production of network materials, a number of 3-dimensional crosslinkable monomers such as, for example, di- and triacrylates are mentioned in EP 0,313,053.

The thickness d of the electrooptical systems is customarily chosen to be small in order achieve a threshold voltage V_{th} which is as low as possible. Thus, for example, layer thicknesses of 0.8 and 1.6 mm are reported in US 4,435,047, while values for the layer thickness between 10 μm and 300 μm are given in US 4,688,900 and between 5 μm and 30 μm in EP 0,313,053. The electrooptical systems according to the invention only have layer thicknesses d which are distinctly greater than a few mm in exceptional cases; layer thicknesses $d \leq 200 \mu\text{m}$, and, in particular, between 10 and 50 μm are preferred.

An essential difference between the composite materials according to the invention and those customary hitherto exists, however, in the liquid crystal mixture used.

The liquid crystal mixtures used in the composite materials according to the invention contain at least one compound of formula I.

The compounds according to formula I exhibit a dielectrically positive or dielectrically neutral terminal group R^3 which is F, Cl, CN or $X-C_1H_5F_{2r+1-s}$ and a dielectrically neutral terminal group



which contains a vinylen-group being embraced by an-optionally substituted - alkyl group R^1 and an - optionally substituted - alkylene group R^2 .

- 5 It was found by the present inventors that composite materials with especially advantageous values of the switching voltages are obtained in case R^1 is CH_3 , C_2H_5 , C_3H_7 , CH_3OCH_2 and very particularly CH_3 .

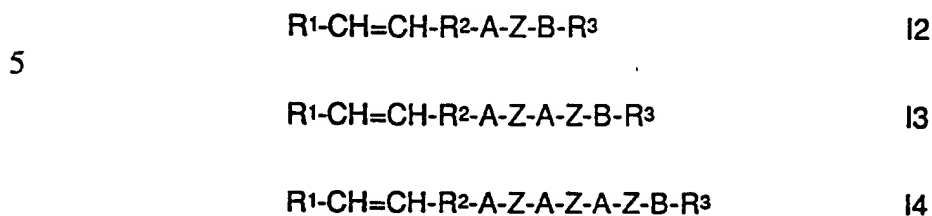
- Especially preferred are the following meanings for $R^1-CH=CH-R^2$:
- 10 2-butenyl, 3-pentenyl, 4-hexenyl, 5-heptenyl, 6-octenyl, 7-nonenyl, 2-butenyloxy, 3-pentenyl, 4-hexenyloxy, 5-heptenyloxy, 6-octenyloxy, 2-oxa-4-hexenyl, 2-oxa-5-heptenyl, 3-oxa-5-heptenyl, 2-oxa-6-octenyl, 3-oxa-6-octenyl, 4-oxa-6-octenyl, 2-butenylcarbonyl, 3-pentenyl-carbonyl, 4-hexenylcarbonyl, 5-heptenylcarbonyl, 6-octenylcarbonyl, 2-butenyl-carbonyloxy, 3-pentenylcarbonyloxy, 4-hexenylcarbonyloxy, 5-heptenyl-carbonyloxy, 2-butenyloxycarbonyl, 3-pentenylloxycarbonyl and 4-hexenyloxy-carbonyl.
- 15

- Further preferred are the following meanings for $R^1-CH=CH-R^2$:
- 20 2-pentenyl, 3-hexenyl, 4-heptenyl, 5-octenyl, 6-nonenyl, 7-decenyl, 2-pentenyl, 3-hexenyloxy, 4-heptenyloxy, 5-octenyloxy, 6-nonenyl, 2-pentenylcarbonyl, 3-hexenyloxycarbonyl, 2-hexenyl, 3-heptenyl, 4-octenyl, 5-nonenyl, 6-decenyl, 7-undecenyl, 2-hexenyloxy, 3-heptenyloxy, 4-octenyloxy, 5-nonenyl, 6-decenyl, 2-hexenylcarbonyl, 2-hexenyloxycarbonyl, 5-oxa-hexenyl, 6-oxa-3-heptenyl, 7-oxa-4-octenyl, 5-oxa-2-hexenyloxy, 6-oxa-3-heptenyloxy, 7-oxa-4-octenyloxy, 5-oxa-2-hexenyloxycarbonyl and 5-oxa-2-hexenylcarbonyloxy.
- 25

- 30 The other terminal group R^3 preferably is a dielectrically positive group, especially F, Cl, CN, CF_3 , OCF_3 , SCF_3 , CHF_2 , $OCHF_2$ and $SCHF_2$, and very particularly F, Cl, CN, CF_3 , OCF_3 and SCF_3 .

- R^3 can also be a dielectrically neutral group, in particular CH_3 , OCH_3 , SCH_3 , C_2H_5 and OC_2H_5 .
- 35

The compounds of formula I include 2-, 3- and 4-ring compounds according to sub-formulae I2, I3 and I4:



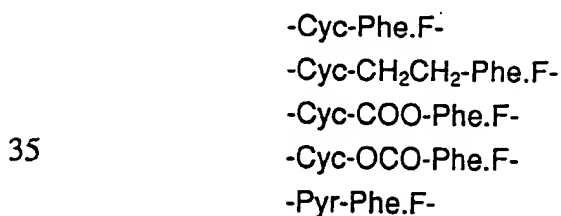
10 In the compounds according to sub-formulae I3 and I4, the ring groups A and the bridging groups Z can be chosen independently from each other.

In the following, for the sake of simplicity, the following abbreviations are used:

15	Cyc	trans-1,4-cyclohexylene
	Phe	1,4-phenylene
	Phe.2F	2-fluoro-1,4-phenylene
	Phe.3F	3-fluoro-1,4-phenylene
20	Phe.3F5F	3,5-difluoro-1,4-phenylene
	Phe.3F6F	3,6-difluoro-1,4-phenylene
	Phe.(F)	is Phe, Phe.2F, Phe.3F, Phe.3F5F or Phe.3F6F
	Phe.F	is Phe.2F, Phe.3F, Phe.3F5F or Phe.3F6F
	Pyr	Pyrimidine-2,5-diyl
25	Pyd	pyridine-2,5-diyl

The acronyms Pyr and Pyd include the two possible positional isomers.

30 In the 2-ring compounds according to sub-formula I2, the mesogenic core -A-Z-B- preferably has the following meaning:



- Pyd-Phe.F-
- Phe.F-Phe.(F)-
- Phe-Phe.F-
- Phe.F-CH₂CH₂-Phe.(F)
- 5 -Phe-CH₂CH₂-Phe.F-
- Phe.F-COO-Phe.(F)
- Phe-COO-Phe.F
- Phe.F-OCO-Phe.(F)
- Phe-OCO-Phe.F

10

Especially preferred is the following smaller group of 2-ring mesogenic cores -A-Z-B-:

- Cyc-Phe.2F-
- 15 -Cyc-Phe.3F-
- Cyc-Phe.3F5F-
- Cyc-CH₂CH₂-Phe.2F
- Cyc-CH₂CH₂-Phe.3F
- Cyc-CH₂CH₂-Phe.3F5F
- 20 -Cyc-CH₂CH₂-Phe.3F6F
- Phe.2F-Phe-
- Phe.3F-Phe-
- Phe.3F5F-Phe-
- Phe-Phe.2F-
- 25 -Phe-Phe.3F-
- Phe-Phe.3F5F-
- Phe-Phe.3F6F-
- Phe.2F-Phe.2F-
- Phe.3F-Phe.2F-
- 30 -Phe.2F-Phe.3F-
- Phe.2F-Phe.3F5F-
- Phe.2F-CH₂CH₂-Phe-
- Phe.3F-CH₂CH₂-Phe-
- Phe.3F5F-CH₂CH₂-Phe-

35

- 14 -

- 5
- Phe-CH₂CH₂-Phe.2F-
 - Phe-CH₂CH₂-Phe.3F-
 - Phe-CH₂CH₂-Phe.3F5F-
 - Phe.2F-CH₂CH₂-Phe.2F-
 - Phe.2F-CH₂CH₂-Phe.3F-
 - Phe.3F-CH₂CH₂-Phe.2F-
 - Phe.2F-CH₂CH₂-Phe.3F5F-
 - Phe.3F5F-CH₂CH₂-Phe.3F5F-
- 10
- Phe-COO-Phe.2F-
 - Phe-COO-Phe.3F-
 - Phe-COO-Phe.3F5F-
 - Phe.2F-COO-Phe.2F-
 - Phe.2F-COO-Phe.3F-
- 15
- Pyr-Phe.2F-
 - Pyr-Phe.3F-
 - Pyr-Phe.3F5F-
 - Pyd-Phe.2F-
 - Pyd-Phe.3F-
 - Pyd-Phe.3F5F-
- 20

In the 3-ring compounds according to sub-formulae I3, the mesogenic core
-A-Z-A-Z-B- preferably has the following meaning:

- 25
- Cyc-Cyc-Phe.F-
 - Cyc-CH₂CH₂-Cyc-Phe.F-
 - Cyc-Cyc-CH₂CH₂-Phe.F
 - Cyc-Phe.F-Phe.(F)-
 - Cyc-Phe-Phe.F-
- 30
- Cyc-CH₂CH₂-Phe.(F)-Phe.F-
 - Cyc-Phe.(F)-CH₂CH₂-Phe.F-
 - Cyc-Phe.F-Cyc-
 - Cyc-C₂H₄-Phe.F-Cyc-
 - Phe.(F)-Phe.F-Phe.(F)-
 - Phe.F-Phe-Phe.(F)-
- 35
- Phe-Phe-Phe.F-

- 15 -

- 5
- Phe.F-Phe.(F)-CH₂CH₂-Phe.(F)-
 - Phe.(F)-CH₂CH₂-Phe.F-Phe.(F)-
 - Phe.F-CH₂CH₂-Phe-Phe.(F)-
 - Phe-CH₂CH₂-Phe-Phe.F-
 - Phe.(F)-COO-Phe.F-(COO)_{0,1}-Phe.(F)-
 - Phe.F-COO-Phe-(COO)_{0,1}-Phe.(F)-
 - Phe-COO-Phe-(COO)_{0,1}-Phe.F-
 - Pyr-Phe.F-Phe.(F)-
 - Pyd-Phe.F-Phe.(F)-

10

Especially preferred is the following smaller group of mesogenic cores with 3 rings -A-Z-A-Z-B:

- 15
- Cyc-Cyc-Phe.2F-
 - Cyc-Cyc-Phe.3F-
 - Cyc-Cyc-Phe.3F5F-
 - Cyc-Cyc-CH₂CH₂-Phe.2F-
 - Cyc-Cyc-CH₂CH₂-Phe.3F-
 - Cyc-Cyc-CH₂CH₂-Phe.3F5F-
- 20
- Cyc-(CH₂CH₂)_{0,1}-Phe.2F-Phe-
 - Cyc-(CH₂CH₂)_{0,1}-Phe.3F-Phe-
 - Cyc-(CH₂CH₂)_{0,1}-Phe.3F5F-Phe-
 - Cyc-(CH₂CH₂)_{0,1}-Phe.2F-Phe.2F-
 - Cyc-(CH₂CH₂)_{0,1}-Phe.2F-Phe.3F-
- 25
- Cyc-(CH₂CH₂)_{0,1}-Phe.3F-Phe.2F-
 - Cyc-(CH₂CH₂)_{0,1}-Phe.3F-Phe.3F-
 - Cyc-(CH₂CH₂)_{0,1}-Phe.3F5F-Phe.2F-
 - Cyc-(CH₂CH₂)_{0,1}-Phe.3F5F-Phe.3F-
- 30
- Cyc-Phe-Phe.2F-
 - Cyc-Phe-Phe.3F-
 - Cyc-Phe-Phe.3F5F-

35

- 5
- Phe-(CH₂CH₂)_{0,1}-Phe.2F-Phe-
 - Phe-(CH₂CH₂)_{0,1}-Phe.3F-Phe-
 - Phe-(CH₂CH₂)_{0,1}-Phe.3F5F-Phe-
 - Phe-(CH₂CH₂)_{0,1}-Phe.3F6F-Phe-
 - Phe.2F-Phe-(CH₂CH₂)_{0,1}-Phe-
 - Phe.3F-Phe-(CH₂CH₂)_{0,1}-Phe-
 - Phe.3F5F-Phe-(CH₂CH₂)_{0,1}-Phe-
 - Phe.3F6F-Phe-(CH₂CH₂)_{0,1}-Phe-
- 10
- Phe-Phe-(CH₂CH₂)_{0,1}-Phe.2F-
 - Phe-Phe-(CH₂CH₂)_{0,1}-Phe.3F-
 - Phe-Phe-(CH₂CH₂)_{0,1}-Phe.3F5F-
 - Phe-Phe-(CH₂CH₂)_{0,1}-Phe.3F6F-
- 15
- Phe.2F-Phe.2F-(CH₂CH₂)_{0,1}-Phe-
 - Phe.3F-Phe.2F-(CH₂CH₂)_{0,1}-Phe-
 - Phe.3F5F-Phe.2F-(CH₂CH₂)_{0,1}-Phe-
 - Phe.2F-Phe.3F-(CH₂CH₂)_{0,1}-Phe-
 - Phe.3F-Phe.3F-(CH₂CH₂)_{0,1}-Phe
 - Phe.3F5F-Phe.3F-(CH₂CH₂)_{0,1}-Phe-
- 20
- Phe-Phe.2F-Phe.2F-
 - Phe-Phe.2F-Phe.3F-
 - Phe-Phe.2F-Phe.3F5F-
 - Phe-Phe.3F-Phe.2F-
 - Phe-Phe.3F-Phe.3F-
- 25
- Phe-Phe.3F-Phe.3F5F-
 - Phe-Phe.3F5F-Phe.2F-
 - Phe-Phe.3F5F-Phe.3F-
 - Phe-Phe.3F5F-Phe.3F5F-

30 In the 4-ring compounds according to subformula I4, the mesogenic core preferably has the following meaning:

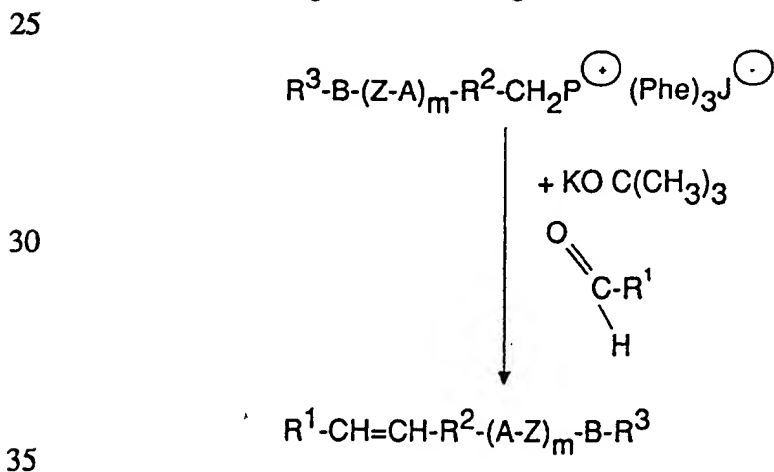
- 35
- Cyc-Cyc-Cyc-(CH₂CH₂)_{0,1}-Phe.F-
 - Cyc-Cyc-(CH₂CH₂)_{0,1}-Phe.F-Phe.(F)-
 - Cyc-Cyc-(CH₂CH₂)_{0,1}-Phe-Phe.F-
 - Cyc-(CH₂CH₂)_{0,1}-Phe.(F)-Phe.F-Phe.(F)-

Especially preferred is the following smaller group of mesogenic cores with 4 rings -A-Z-A-Z-A-Z-B:

- 5 -Cyc-Cyc-Cyc-Phe.2F-
 -Cyc-Cyc-Cyc-Phe.3F-
 -Cyc-Cyc-Cyc-Phe.3F5F-
 -Cyc-Cyc-Phe.2F-Phe-
 -Cyc-Cyc-Phe.3F-Phe-
 10 -Cyc-Cyc-Phe.3F5F-Phe-
 -Cyc-Phe-Phe.2F-Phe-
 -Cyc-Phe-Phe.3F-Phe-
 -Cyc-Phe-Phe.3F5F-Phe-

15 The compounds of formula I are prepared by methods which are known per se, such as are described in the literature (for example in the standard works such as Houben-Weyl, Methoden der Organischen Chemie (Methods of Organic Chemistry), Georg-Thieme-Verlag, Stuttgart), and in particular under reaction conditions which are known and suitable for the reactions mentioned. In these reactions, it is also possible to utilize
 20 variants which are known per se and are not mentioned here in more detail.

25 The compounds of formula I can be obtained, for example, via a Wittig reaction according to the following scheme



It is further possible to convert appropriate $R^1\text{-CH=CH-R}^2$ -terminal substituted precursors to the compounds of formula I via a metal-catalyzed cross-coupling reaction as is described, for example, in E. Poetsch, Kontakte, Darmstadt, 1988 (2), p. 15ff.

5

Other methods of preparing compounds of formula I are apparent to those skilled in the art.

10

The liquid crystal materials used in the composite materials according to the invention preferably contain 1-50 %, particularly preferably 5-45 % of one or more compounds according to formula I. The liquid crystal materials preferably contain 1-10, in particular 1-5 compounds according to formula I.

15

The liquid crystal materials according to the invention preferably contain 2-40, in particular 4-30 and especially 6-30 compounds. The liquid crystal materials preferably contain 1-20 and especially 1-15 compounds other than those of formula I.

20

These other compounds are preferably chosen from the nematic or nematogenic (monotropic or isotropic) substances, in particular substances from the classes of azoxybenzenes, benzylideneanilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, phenyl or cyclohexylcyclohexanecarboxylates, phenyl or cyclohexyl esters of

25

cyclohexylbenzoic acid, phenyl or cyclohexyl esters of cyclohexylbenzoic acid, phenyl or cyclohexyl esters of cyclohexylcyclohexanecarboxylic acid, phenylcyclohexanes, cyclohexylbiphenyls, phenylcyclohexylcyclohexanes, cyclohexylcyclohexanes, cyclohexylcyclohexenes,

30

cyclohexylcyclohexylcyclohexenes, 1,4-bis-cyclohexylbenzenes, 4,4'-bis-cyclohexylbiphenyls, phenyl- or cyclohexylpyrimidines, phenyl- or cyclohexylpyridines, phenyl- or cyclohexyldioxanes, phenyl- or cyclohexyl-1,3-dithianes, 1,2-diphenylethanes, 1,2-dicyclohexylethanes, 1-phenyl-2-

35

cyclohexylethanes, 1-cyclohexyl-2-(4-phenyl-cyclohexyl)-ethanes, 1-cyclohexyl-2-biphenylethanes, 1-phenyl-2-cyclohexylphenylethanes, optionally halogenated stilbenes, benzyl phenyl ethers, tolanes and substituted cinemetic acids. The 1,4-phenylene groups in these compounds can also be fluorinated.

The most important compounds which can further be contained in liquid crystal materials to be used in the composite materials, can be characterized by the formulae 1, 2, 3, 4 and 5:

$R'-L-E-R''$	1
$R'-L-COO-E-R''$	2
$R'-L-OOC-E-R''$	3
$R'-L-CH_2CH_2-E-R''$	4
$R'-L-C\equiv C-E-R''$	5

In the formulae 1, 2, 3, 4 and 5, L and E, which can be identical or different, in each case independently of one another are a bivalent radical from the group comprising -Phe-, -Cyc-, -Phe-Phe-, -Phe-Cyc-, -Cyc-Cyc-, -Pyr-, -Dio-, -G-Phe- and -G-Cyc- and mirror images thereof, wherein Phe is 1,4-phenylene which is unsubstituted or substituted by fluorine, Cyc is trans-1,4-cyclohexylene or 1,4-cyclohexenylene, Pyr is pyrimidine-2,5-diyl or pyridine-2,5-diyl, Dio is 1,3-dioxane-2,5-diyl and G is 2-(trans-1,4-cyclohexyl)-ethyl, pyrimidine-2,5-diyl, pyridine-2,5-diyl or 1,3-dioxane-2,5-diyl.

Preferably, one of the radicals L and E is Cyc, Phe or Pyr. E is preferably Cyc, Phe or Phe-Cyc. The media according to the invention preferably contain one or more components chosen from the compounds of the formulae 1, 2, 3, 4, and 5, wherein one of the radicals L and E is chosen from the group comprising Cyc, Phe and Pyr and the other radical is chosen from the group comprising -Phe-Phe-, -Phe-Cyc-, -Cyc-Cyc-, -G-Phe- and -G-Cyc-, and if appropriate one or more components chosen from the compounds of the formulae 1, 2, 3, 4 and 5 wherein the radicals L and E are chosen from the group comprising -Phe-Cyc-, -Cyc-Cyc-, -G-Phe- and -G-Cyc-.

5 In a smaller subgroup of part formulae 1a, 2a, 3a, 4a and 5a, R' and R" in each case independently of one another are alkyl, alkenyl, alkoxy, alkenyloxy or alkanoyloxy having up to 8 carbon atoms. In most of these compounds, R' and R" differ from one another, one of these radicals usually being alkyl or alkenyl. In the compounds of another smaller subgroup of the part formulae 1b, 2b, 3b, 4b and 5b, R" is -CN, -CF₃, OCF₃, SCF₃, OCHF₂, CHF₂, SCHF₂, F, Cl or -NCS; R here has the meaning given in the case of the compounds of the part formulae 1a to 5a, and is preferably alkyl or alkenyl. However, other variants of the envisaged substituents in 10 the compounds of the formulae 1, 2, 3, 4 and 5 can also be used.

15 Many such substances or mixtures thereof are commercially available. All these substances are obtainable by methods which are known from the literature or by analogous methods.

20 The liquid crystal materials to be used in the composite materials according to the invention preferably also contain, in addition to components from the group of compounds 1a, 2a, 3a, 4a and 5a (group 1), components from the group of compounds 1b, 2b, 3b, 4b and 5b (group 2), the proportions of which are preferably as follows:

Group 1: 20 to 70 %, in particular 30 to 60 %,

Group 2: 10 to 90 %, in particular 10 to 75 %,

25 the sum of the proportion of the compounds according to formula I and the compounds from groups 1 and 2 being up to 100 %.

30 The liquid crystal mixtures to be used according to the invention can be modified by further additives in such a way that they can be used in all electrooptical systems containing a composite material according to claim 1.

35

Additives of this type are known to the person skilled in the art and are described in detail in the literature. Thus, for example, pleochroitic dyes can be added for the preparation of coloured electrooptical systems or substances can be added to change the dielectric anisotropy, the optical anisotropy, the viscosity and/or the temperature dependence of electrooptical parameters of the liquid crystals. Substances of this type are described, for example, in H. Kelker and R. Hatz, Handbook of Liquid Crystals, Verlag Chemie, Weinheim, 1980 and in DE-OS 2,209,127, 2,240,864, 2,321,632, 2,338,281, 2,450,088, 2,637,430, 2,853,728 and 2,902,177.

Electrooptical systems in which pleochroitic dyes are added to the liquid crystal material in a per cent by weight range of 0-25 %, in particular 0-20 % and very particularly 0-15 % are preferred.

In addition, chiral mesogenic or, alternatively, non-mesogenic compounds can be added to the liquid crystal mixtures to increase the scattering of the electrooptical system in the opaque state and/or to influence the slope of the electrooptical curve, as is described, for example, in DE 4,007,039. Liquid crystals according to the invention which contain 0-15 % and in particular 0-10 % of chiral additives are preferred.

It was found out by the present inventors that the liquid crystal materials containing at least one compound of formula I can be used with most precursors of the polymeric medium hitherto known. This was especially surprising with respect to photoradically curable precursors based on vinyl type compounds like those disclosed in EP 0,272,585, WO 93-09,202 or in the PCT application No. WO 93-01,378 filed by the present applicant on June 02, 1993.

It turned out that in particular composite materials the precursor of which is based on acrylate type monomers, oligomers and/or prepolymers, exhibit advantageous properties and composite materials of this type are preferred. It has to be assumed - though the present inventors do not wish to be restricted to this explanation - that the reactivity of the acrylate type components of the precursor with respect to photopolymerization is

distinctly higher than that of the liquid crystal compounds according to formula I so that a polymerization of the compounds of formula I takes place to a negligible degree only. In co-pending PCT application No. WO 93-00,989 filed on April 23, 1993 by the present applicant, it is shown

5 that the addition of a small amount of reactive, i.e. polymerizable liquid crystal compounds to a liquid crystal mixture results in a distinct improvement of switching times and a tolerable deterioration of switching voltages. The composite materials according to the present invention are characterized by rather low to low values of switching voltage and by

10 advantageous values of switching times so that the present inventors further assume that in case a small part of the compounds according to formula I takes part in the polymerization reaction, the resulting deterioration of switching voltage is at least partly or even over-

15 compensated by the decrease of switching voltages caused by the presence of unreacted compounds of formula I in the liquid crystal mixture.

The present inventors further found that compounds according to formula I with a terminal vinyl group ($R^1 = H$) exhibit a comparably high reactivity in photopolymerization reactions and are less suited for photo-curable

20 composite materials; contrary to this they can be used in thermally curable composite materials such as, for example, epoxy based materials. PDLC and PN systems, for example, the liquid crystal mixture of which contains compounds of formula I with a comparably high reactivity, can be obtained by applying TIPS or SIPS technique.

25 Composite materials with especially advantageous properties are obtained if the liquid crystal material contains at least one compound according to formula I wherein the double bond is in the position next to the terminal C-C-bond of the group $R^1-CH=CH-R^2$, i.e.

30



35

Liquid crystal materials of this type were found to exhibit an acceptable to low reactivity in the photopolymerization reaction, and electrooptical systems containing a composite material with such a liquid crystal material exhibit low to very low switching voltages.

5

Especially preferred are composite materials and electrooptical systems with a liquid crystal material the component consisting of one or more compounds of formula I of which is based on compounds exhibiting the preferred position of the vinylen group according to formula (a); this component preferably contains more than 30 % and, in particular, 50-100 % of one or more compounds with a vinylen group according to formula (a).

10

Liquid crystal materials containing one or more compounds according to formula I with a "more inner" (that is with a greater number of carbon atoms in R¹) vinylen group

15



with R¹ being alkyl with 2-6 C atoms wherein one or two CH₂-groups can be replaced by -O- or -CO-, are furthermore preferred, in particular for use in photocurable precursors of the transparent medium.

20

The precursor of the polymer is preferably based on an ene-type component comprising one or more olefinically unsaturated monomers and/or oligomers.

25

Preferred is the following smaller group of olefinically unsaturated monomers which is to illustrate the invention without restricting it:

30

vinyl chloride, vinylidene chloride, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, methylacrylate or methacrylate, ethylacrylate or methacrylate, n- or tert-butylacrylate or methacrylate, cyclohexylacrylate or methacrylate, 2-ethylhexylacrylate or methacrylate, benzylacrylate or methacrylate, phenyloxyethylacrylate or methacrylate, hydroxyethylacrylate or methacrylate, hydroxypropylacrylate or methacrylate, lower

35

alkoxyethylacrylate or methacrylate, tetrahydrofurfuryl acrylate or methacrylate, vinyl acetate, vinyl propionate, vinyl acrylate, vinyl succinate, N-vinylpyrrolidone, N-vinylcarbazole, styrene, divinylbenzene, ethylene diacrylate, 1,6-hexandiol diacrylate, bisphenol A diacrylate and dimethacrylate, trimethylolpropane diacrylate, pentaerythritol triacrylate, triethylene glycol diacrylate, ethylene glycol dimethacrylate, tripropylene glycol triacrylate, pentaerythritol triacrylate, pentaerythritol tetracrylate, ditrimethylpropane tetraacrylate and dipentaerythritol pentaacrylate or hexaacrylate.

Especially preferred are acrylate type compound.

Examples for olefinically unsaturated oligomers are the commercially available oligomers Ebecryl 270 (aliphatical urethane/diacrylate), Ebecryl 1810 (polyester/tetraacrylate) and/or Ebecryl 600 (bisphenol-A-epoxy/diacrylate). Other oligomers can be used, and the examples given are to illustrate the invention without limiting it.

The mass ratio of the ene-type component with respect to the mass of the precursor of the polymer matrix preferably amounts to 5-99 % and, in particular, to 15-90 %.

The precursor of the polymer matrix can contain polymerizable monomers and/or oligomers other than ene-type compounds like, for example, compounds with two or more hydroxyl groups, two or more isocyanate groups, a hydroxyl group and/or an isocyanate group and another polymerizable groups or other compounds in order to influence and optimize the properties of the precursor and the cured polymer matrix.

Especially preferred as further components of the precursor of the polymer matrix are di- or higher functional thiol monomers and/or oligomers (= compounds with at least two SH-groups). Preferred examples of thiol monomers can be taken from the following list:

2,2-dimercaptodiethyl ether, glycol dimercaptoacetate, glycol dimercapto-
propionate (also termed ethylene bis(3-mercaptopropionate),
pentaerythritol tetra (3-mercaptopropionate), pentaerythritol
tetrathioglycolate, trimethylolethane, tri(3-mercaptopropionate),
5 trimethylolethane trithioglycolate, trimethylolpropane tri (3-mercaptopropionate), trimethylolpropane trithioglycolate, dipentaerythritol hexa(3-mercaptopropionate), polyethylene glycol dimercaptoacetate, and polyethylene glycol di(3-mercaptopropionate).

10 Precursor of the polymer matrix containing one or more thiol monomers and/or oligomers are preferred because the formation of the correct Swiss cheese morphology is distinctly favoured by adding a thiol component.

15 The mass ratio of the thiol component preferably is not too high, especially not more than 50 % and, in particular, less than 25 % with respect to the mass of the precursor of the matrix. If the amount of the thiol component is chosen too high this often adversely affects the solubility of the liquid crystal mixture in the precursor.

20 The precursor of the polymer matrix can contain other components such as, for example, softening agents, stabilizing agents or other additives customary in the field of polymers.

25 The composite materials according to the present invention and the electrooptical systems containing them, are characterized by advantageous properties and, in particular, by rather low to low switching voltages. The composite materials according to the present invention are therefore especially preferred for display applications, but also for further applications.

30

35

Examples

10 % of nematic liquid crystal single compounds were added to a liquid crystal medium (LCI) consisting of:

5

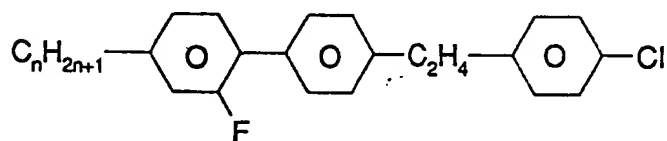
FET-2CL	17.5 %
FET-3CL	9.0 %
FET-5CL	23.5 %
T-3FCLF	13.8 %
10 T-5FCLF	15.3 %
T-3FFF	9.7 %
BCH-5F.F	11.2 %

wherein the codes mean:

15

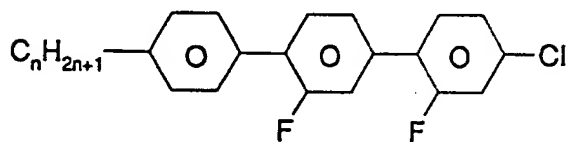
FET-nCL

20



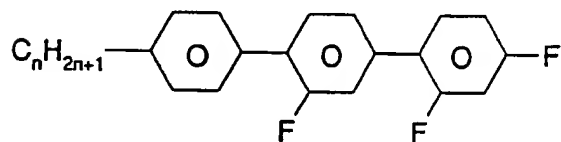
T-nFCLF

25



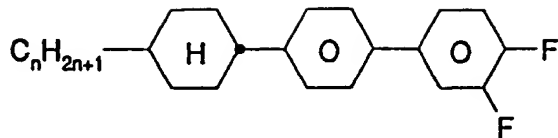
T-nFFF

30

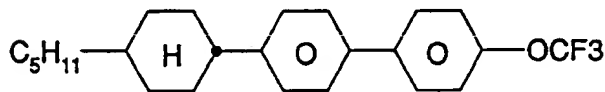


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BCH-nF.F

Comparative Example 1

10 % of BCH-5OCF3 with the chemical code

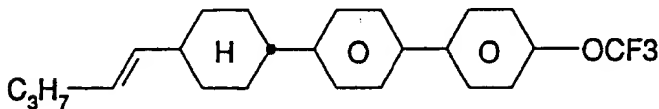


15 have been added to LCI

The properties of the resulting composition are listed in table 1 below.

Example 1

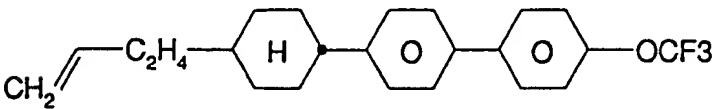
20 10 % of M1 with the code



have been added to LCI, the physical properties are of the resulting mixture (LC III) are given in table 1.

Example 2

30 10 % of M2 with the code



have been added to LCI, the physical properties of the resulting mixture (LC IV) are included in table 1.

The data of table 1 show that M1 is increasing the birefringence of the medium, compared to BCH-5OCF3.

Table 1

Physical properties of LCs

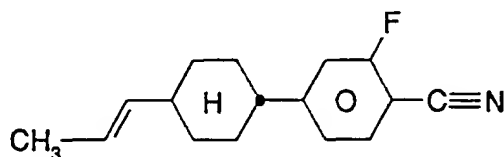
Example LC	Comp. Ex 1 LC II	Ex 1 LC III	Ex 2 LC IV
T (N,I)/°C	92.6	92.6	91.6
Δn	0.2220	0.2231	0.2218
n_e	1.7420	1.7434	1.7432
n_o	1.5200	1.5203	1.5214
Composition c/%			
LCI	90	90	90
BCH-5OCF3	10	-	-
M1	-	10	-
M2	-	-	10

Example 3 to 16

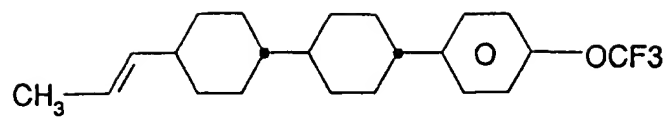
10 % each of the compounds M3 to M16 individually have been added to LC I as in example 1.

This codes M3 to M16 are representing the compounds

M3

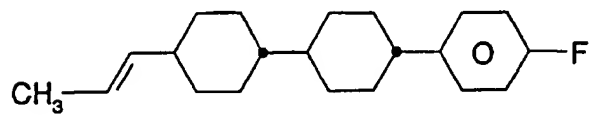


M4



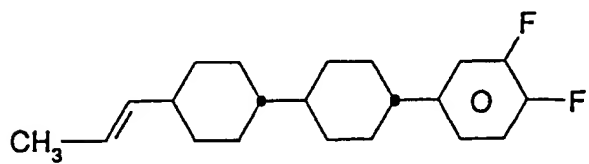
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M5



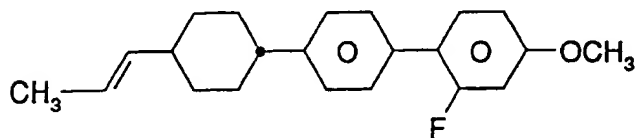
10

M6

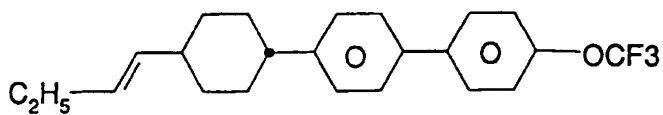


15

M7

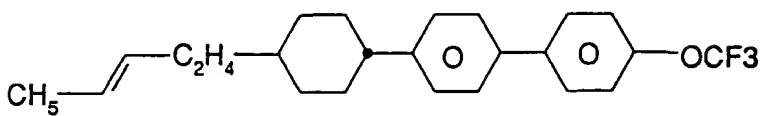


M8



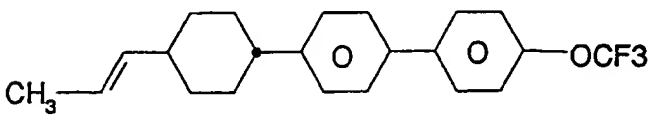
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M9



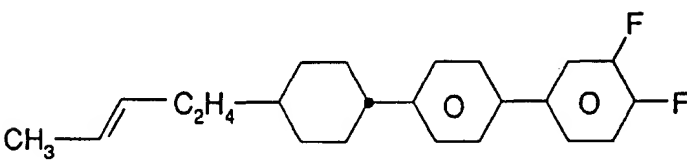
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M10



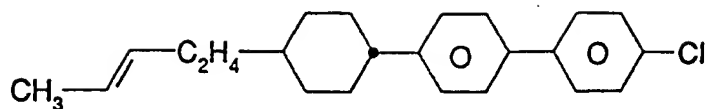
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M11



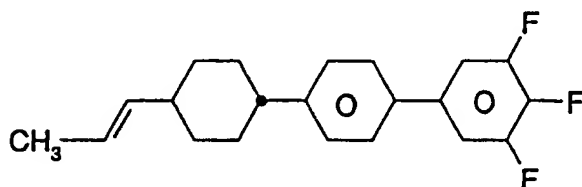
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M12



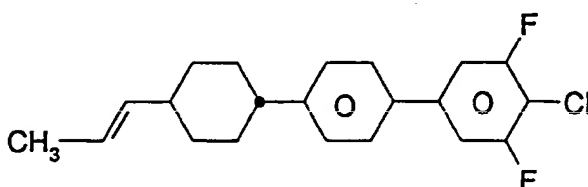
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M13



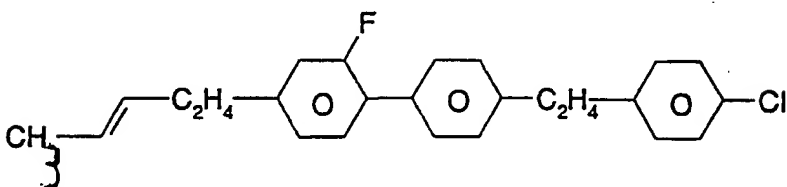
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M14



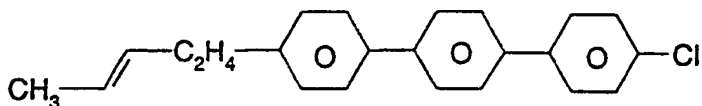
15

M15



20

M16



Use Examples

25

PDLC films have been made from the 17 liquid crystal mixtures using the 17 compounds described above (BCH-5OCF₃ and M 1 to M 16). 80 % of the LC materials were mixed with 20 % of the polymer precursor PN 393, available through Merck Ltd. GB and filled in test cells with ITO electrodes having a cell gap of 10 μm. All films were UV cured at 30 °C and 4.7 mWcm⁻² power. All 17 compositions yielded PDLC films which were

30

35

opaque in the undriven state. The properties of the films of the comparative example 1 and of examples 1 and 2 are summarized in the following table 2.

5 Table 2

Physical properties of PDLC films

10	Use Example	Comp. Ex 1	Ex 1	Ex 2
	Liquid crystal	LC II	LC III	LC IV
	Concentration/%	80	80	80
	Polymer precursor	PN 393	PN 393	PN 393
15	Concentration/%	20	20	20
	T_{off}	0.0076	0.0099	0.0101
	T_{on}	0.7437	0.7497	0.6647
	V_{90}/V	22.4	23.6	49.0
	Contrast ratio	97.71	76.71	65.98
20	$T(N-I)$ of PDLC film/ $^{\circ}C$	86.9	85.5	83.5

The results shown in table 2 show that it is possible to achieve PDLC films from the materials with unsaturated alkyl chains. The PDLC film of the example 1 (LC III) performs similarly to the film of comparative example 1 (LCII) indicating almost no participation of the unsaturated compound M1 in the polymerization. Whereas the high saturation voltage (V_{90}) and the poor contrast of the example 2 (LC IV) is likely due to a significant participation of M2 in the polymerization, leading to an incorporation of M2 into the polymer, which is also supported by the lowered clearing point of the film.

The films obtained with the liquid crystal mixtures containing the compounds M 3 to M 16 (LC V to LC XVIII) are characterized by low off state transmissions, good contrast ratio and low operation voltages.

Patent claims

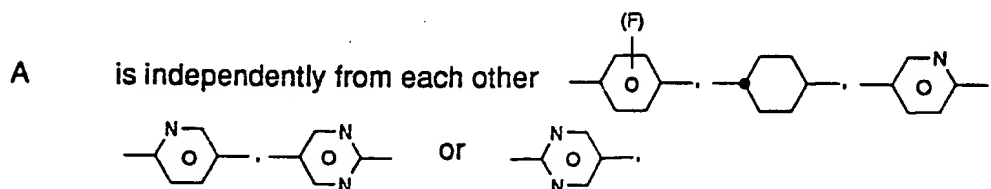
1. Composite material, comprising a liquid crystal material with a birefringence $\Delta n = n_e - n_o$, and a polymeric medium, which is optically substantially transparent and isotropic and has a refractive index of n_m , the liquid crystal material being embedded in microdroplets in the polymeric medium with one of the refractive indices of the liquid crystal material being substantially matched to the refractive index n_m of said polymeric medium, or the liquid crystal material being present as a substantially continuous phase in a 3-dimensional network formed by or with the polymeric medium, characterized in that the liquid crystal material contains at least one compound of formula I



wherein

R^1 is alkyl with 1-6 C atoms, wherein one or two CH_2 -groups can be replaced by -O- or -CO-,

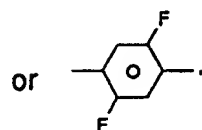
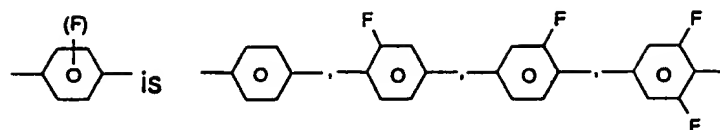
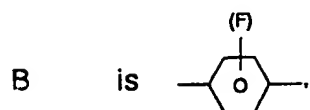
R^2 is alkylene $-(CH_2)_p-$ with p ranging from 1-6, wherein one or two CH_2 -groups can be replaced by -O- or -CO-,



Z is independently from each other a single bond, $-CH_2-CH_2-$, $-COO-$ or $-OCO-$,

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m is 1, 2 or 3,



R³ is F, Cl, CN, X-C₇H₅F_{2+1-s},

X is a single bond, -O- or -S-,

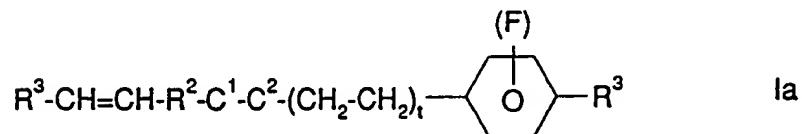
r is 1 or 2,

s is 0, 1, 2, 3, 4 or 5

with the proviso that at least one of A and B is a laterally mono- or difluorinated 1,4-phenylene group.

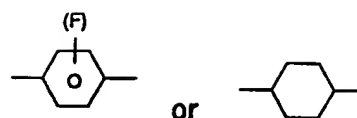
2. Composite material according to claim 1, wherein R¹ is methyl.

3. Composite material according to claim 1 or 2, characterized in that the liquid crystal mixture contains at least one compound of formula Ia



C¹ and

C² is independently from each other



or

5

t is 0 or 1, and

R¹, R², R³ and



10

with the proviso that at least one of the rings is a laterally mono- or difluorinated 1,4-phenylene group.

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4. Composite material according to claims 1-3, wherein the percentage of the liquid crystal material with respect to the mass of the composite materials varies between 30-95 wt%.

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5. Precursor of the composite material according to claims 1-3, comprising a liquid crystal material containing at least one compound of formula I and a UV-curable precursor of the polymeric medium.

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6. Electrooptical system with electrically switchable transparency containing a film of the composite material according to claims 1-4 between 2 electrode layers.

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-35-

Relevant Technical Fields

(i) UK Cl (Ed.M) C4X (X12)
(ii) Int Cl (Ed.5) C09K 19/00

Search Examiner
MR S J QUICK

Date of completion of Search
8 NOVEMBER 1994

Documents considered relevant
following a search in respect of
Claims :-
1-6 (in part)

DATABASES SEARCHED

ONLINE DATABASES: CAS ONLINE

Categories of documents

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|---|---|
| X: Document indicating lack of novelty or of inventive step. | P: Document published on or after the declared priority date but before the filing date of the present application. |
| Y: Document indicating lack of inventive step if combined with one or more other documents of the same category. | E: Patent document published on or after, but with priority date earlier than, the filing date of the present application. |
| A: Document indicating technological background and/or state of the art. | &: Member of the same patent family; corresponding document. |

Category	Identity of document and relevant passages	Relevant to claim(s)
A,P	WO 93/22397 A1 (MERCK PATENT) 11.11.93, see Claim 1; acknowledged in this application	1-6
X	WO 91/05029 A1 (MERCK PATENT) 18.04.91, see abstract and Claim 1 at least; acknowledged in this application	1-6

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